

CLAIMS:

[c01] 1. A method for preparing an aromatic polyether polymer which comprises contacting, in a solvent of low polarity, substantially equimolar amounts of at least one alkali metal salt of a dihydroxy-substituted aromatic hydrocarbon and at least one bis((N-(chlorophthalimido))aromatic compound, in the presence of a phase transfer catalyst which is substantially stable at the temperatures employed; said method further comprising at least one of the following embodiments:

(A) employing substantially dry solvent, alkali metal salt and bis(N-(chlorophthalimido))aromatic compound such that the reaction mixture comprising the same contains at most about 20 ppm by weight of water;

(B) starting the reaction by addition of phase transfer catalyst wherein the polymer solids level in said solvent is at a value of at least about 15% and then concentrating the mixture during reaction until the said value is in the range of between about 25% polymer solids level and about 60% polymer solids level;

(C) maintaining the combined level of said alkali metal salt and bis(N-(chlorophthalimido))aromatic compound in said solvent at a value in the range of between about 25% polymer solids level and about 60% polymer solids level;

(D) beginning said contact using a molar excess of said bis(N-(chlorophthalimido))aromatic compound up to about 5% and subsequently adding alkali metal salt at least once to afford a polyether polymer of a desired molecular weight;

(E) employing alkali metal salt having less than about 25% of particles with a diameter of greater than about 200 nm; and

(F) employing at least one of

(1) an alkali metal salt which is stoichiometrically pure or contains at most about 0.3 mole % of free dihydroxy-substituted aromatic hydrocarbon or of free sodium hydroxide, and

(2) a bis(N-(chlorophthalimido))aromatic compound which is stoichiometrically pure or contains excess anhydride groups in a proportion up to 0.5 mole %, contains phthalides in a proportion no greater than about 1000 ppm, and contains chlorobenzoic acids in a proportion no greater than about 0.15 mole %.

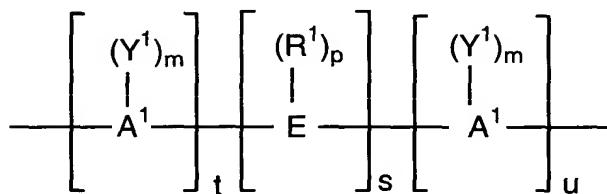
[c02] 2. The method according to claim 1 wherein the solvent is at least one member selected from the group consisting of o-dichlorobenzene, dichlorotoluene, 1,2,4-trichlorobenzene, diphenyl sulfone, phenetole, anisole and veratrole.

[c03] 3. The method according to claim 2 wherein the solvent is ortho-dichlorobenzene.

[c04] 4. The method according to claim 1 wherein the alkali metal salt is derived from at least one dihydroxy-substituted aromatic hydrocarbon of the formula



wherein D has the structure of formula:



wherein A¹ represents an aromatic group;

E comprises a sulfur-containing linkage, sulfide, sulfoxide, sulfone; a phosphorus-containing linkage, phosphinyl, phosphoryl; an ether linkage; a carbonyl group; a tertiary nitrogen group; a silicon-containing linkage; silane; siloxy; a cycloaliphatic group; cyclopentylidene, cyclohexylidene, 3,3,5-trimethylcyclohexylidene, methylcyclohexylidene, 2-[2.2.1]-bicycloheptylidene, neopentylidene, cyclopentadecylidene, cyclododecylidene, adamantlylidene; an alkylene or alkylidene group, which group may optionally be part of one or more fused rings attached to one or more aromatic groups bearing one hydroxy substituent; an unsaturated alkylidene group; or two or more alkylene or alkylidene groups connected by a moiety different from alkylene or alkylidene and selected from the

group consisting of an aromatic linkage, a tertiary nitrogen linkage; an ether linkage; a carbonyl linkage; a silicon-containing linkage, silane, siloxy; a sulfur-containing linkage, sulfide, sulfoxide, sulfone; a phosphorus-containing linkage, phosphinyl, and phosphonyl;

R^1 comprises hydrogen; a monovalent hydrocarbon group, alkenyl, allyl, alkyl, aryl, aralkyl, alkaryl, or cycloalkyl;

Y^1 independently at each occurrence is selected from the group consisting of an inorganic atom, a halogen; an inorganic group, a nitro group; an organic group, a monovalent hydrocarbon group, alkenyl, allyl, alkyl, aryl, aralkyl, alkaryl, cycloalkyl, and an alkoxy group;

the letter "m" represents any integer from and including zero through the number of positions on A^1 available for substitution;

the letter "p" represents an integer from and including zero through the number of positions on E available for substitution;

the letter "t" represents an integer equal to at least one;

the letter "s" represents an integer equal to either zero or one; and

"u" represents any integer including zero

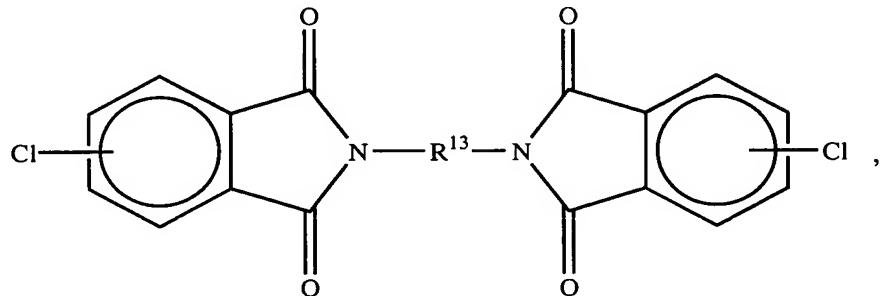
[c05] 5. The method according to claim 1 wherein the alkali metal salt is derived from at least one dihydroxy-substituted aromatic hydrocarbon selected from the group consisting of 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol; 4,4'-bis(3,5-dimethyl)diphenol, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane; 4,4-bis(4-hydroxyphenyl)heptane; 2,4'-dihydroxydiphenylmethane; bis(2-hydroxyphenyl)methane; bis(4-hydroxyphenyl)methane; bis(4-hydroxy-5-nitrophenyl)methane; bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane; 1,1-bis(4-hydroxyphenyl)ethane; 1,2-bis(4-hydroxyphenyl)ethane; 1,1-bis(4-hydroxy-2-chlorophenyl)ethane; 2,2-bis(4-hydroxyphenyl)propane; 2,2-bis(3-phenyl-4-hydroxyphenyl)propane; 2,2-bis(4-hydroxy-3-methylphenyl)propane; 2,2-bis(4-hydroxy-3-ethylphenyl)propane; 2,2-bis(4-hydroxy-3-isopropylphenyl)propane; 2,2-

bis(4-hydroxy-3,5-dimethylphenyl)propane; 3,5,3',5'-tetrachloro-4,4'-dihydroxyphenyl)propane; bis(4-hydroxyphenyl)cyclohexylmethane; 2,2-bis(4-hydroxyphenyl)-1-phenylpropane; 2,4'-dihydroxyphenyl sulfone; dihydroxy naphthalene, 2,6-dihydroxy naphthalene; hydroquinone; resorcinol; C₁₋₃ alkyl-substituted resorcinols; 2,2-bis-(4-hydroxyphenyl)butane; 2,2-bis-(4-hydroxyphenyl)-2-methylbutane; 1,1-bis-(4-hydroxyphenyl)cyclohexane; bis-(4-hydroxyphenyl); bis-(4-hydroxyphenyl)sulphide; 2-(3-methyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane; 2-(3,5-dimethyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane; 2-(3-methyl-4-hydroxyphenyl)-2-(3,5-dimethyl-4-hydroxyphenyl)propane; bis-(3,5-dimethylphenyl-4-hydroxyphenyl)methane; 1,1-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)ethane; 2,2-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)propane; 2,4-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)-2-methylbutane; 3,3-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)pentane; 1,1-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)cyclopentane; 1,1-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)cyclohexane; bis-(3,5-dimethylphenyl-4-hydroxyphenyl)sulphide, 3-(4-hydroxyphenyl)-1,1,3-trimethylindan-5-ol, 1-(4-hydroxyphenyl)-1,3,3-trimethylindan-5-ol, 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indene]-6,6'-diol, and mixtures thereof.

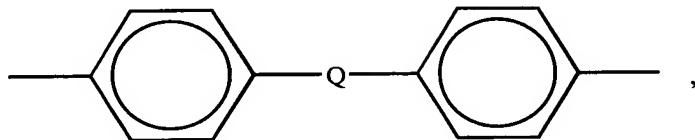
[c06] 6. The method according to claim 5 wherein the alkali metal salt is derived from bisphenol A.

[c07] 7. The method according to claim 6 wherein the bisphenol A salt is the disodium salt.

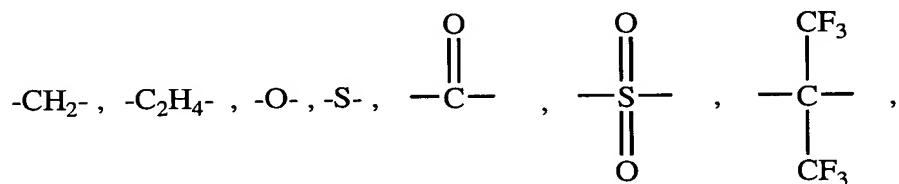
[c08] 8. The method according to claim 1 wherein the bis(N-(chlorophthalimido))aromatic compound has the formula



wherein R¹³ comprises a C₆₋₂₂ divalent aromatic hydrocarbon or halogenated hydrocarbon radical, a C₂₋₂₂ alkylene or cycloalkylene radical or a divalent radical of the formula



in which Q is a covalent bond or a member selected from the group consisting of



and an alkylene or alkylidene group of the formula C_yH_{2y}, wherein y is an integer from 1 to 5 inclusive.

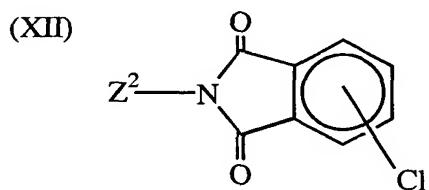
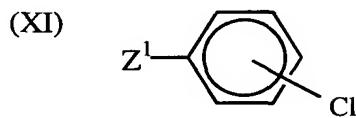
[c09] 9. The method according to claim 8 wherein R¹³ is derived from at least one diamine selected from the group consisting of meta-phenylenediamine; para-phenylenediamine; 2-methyl-4,6-diethyl-1,3-phenylenediamine; 5-methyl-4,6-diethyl-1,3-phenylenediamine; bis(4-aminophenyl)-2,2-propane; bis(2-chloro-4-amino-3,5-diethylphenyl)methane, 4,4'-diaminodiphenyl, 3,4'-diaminodiphenyl, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 2,4-toluenediamine; and mixtures thereof.

[c10] 10. The method according to claim 1 wherein the phase transfer catalyst is a hexaalkylguanidinium salt.

[c11] 11. The method according to claim 10 wherein the hexaalkylguanidinium salt is a chloride.

[c12] 12. The method according to claim 1 wherein there is also present a chain termination agent.

[c13] 13. The method according to claim 12 wherein the chain termination agent is at least one member selected from the group consisting of alkyl halides, alkyl chlorides, aryl halides, aryl chlorides, compounds of formula (XI) and compounds of formula (XII):



wherein the chlorine substituent is in the 3- or 4-position, and Z^1 and Z^2 comprise a substituted or unsubstituted alkyl or aryl group.

[c14] 14. The method according to claim 12 wherein the chain termination agent comprises at least one of 4-chloro-N-methylphthalimide, 4-chloro-N-butylphthalimide, 4-chloro-N-octadecylphthalimide, 3-chloro-N-methylphthalimide, 3-chloro-N-butylphthalimide, 3-chloro-N-octadecylphthalimide, 4-chloro-N-phenylphthalimide, 3-chloro-N-phenylphthalimide, 1-N-(4-chlorophthalimido)-3-(N-phthalimido)benzene, 1-N-(3-chlorophthalimido)-3-(N-phthalimido)benzene, 4-N-(3-chlorophthalimido)phenyl-4'-(N-phthalimido)phenyl ether, 4-N-(4-chlorophthalimido)phenyl-4'-(N-phthalimido)phenyl ether, or the corresponding isomers derived from 3,4'-diaminodiphenyl ether, wherein any mono-substituted bis-phthalimide chain termination agent is optionally in admixture with bis-substituted bis-phthalimide monomer.

[c15] 15. The method according to claim 1 comprising embodiment A.

[c16] 16. The method according to claim 15 wherein the alkali metal salt, in combination with a portion of solvent, is dried to a water content of at most about 20 ppm, and the bis(N-(chlorophthalimido))aromatic compound, in combination with a portion of solvent and, optionally with chain termination agent, is dried to a water content of at most about 20 ppm.

[c17] 17. The method according to claim 16 wherein drying is by distillation.

[c18] 18. The method according to claim 15 wherein the bis(N-(chlorophthalimido))aromatic compound, at least a portion of solvent and at least a portion of phase transfer catalyst, optionally predried separately, are combined and, optionally, further dried by distillation until the value of about 20 ppm water or less is attained; followed by addition of dry alkali metal salt to the mixture, wherein the initial solids level of the mixture is at least about 15% and the solids level following complete addition of salt and optional concentration is in a range of between about 15% and about 35%.

[c19] 19. The method according to claim 1 comprising embodiment B.

[c20] 20. The method according to claim 19 wherein the polymer solids level in said solvent is at a value of at least about 25% before starting the reaction by addition of phase transfer catalyst and wherein the mixture is concentrated during reaction until the said value is in the range of between about 30% polymer solids level and about 40% polymer solids level.

[c21] 21. The method according to claim 1 comprising embodiment C.

[c22] 22. The method according to claim 21 wherein said combined level is in the range of between about 30% solids level and about 40% solids level.

[c23] 23. The method according to claim 21 wherein cyclic oligomer levels are less than about 4 wt. %.

[c24] 24. The method according to claim 21 wherein cyclic oligomer levels are less than about 3 wt. %.

[c25] 25. The method according to claim 1 comprising embodiment D.

[c26] 26. The method according to claim 25 wherein the initial molar excess of bis(N-(chlorophthalimido))aromatic compound is in the range of between about 0.75% and about 3%.

[c27] 27. The method according to claim 1 comprising embodiment E.

[c28] 28. The method according to claim 27 wherein the alkali metal salt has less than about 5% of particles with a diameter of greater than about 500 nm.

[c29] 29. The method according to claim 27 wherein the alkali metal salt has less than about 2% of particles with a diameter of greater than about 500 nm.

[c30] 30. The method according to claim 27 wherein the alkali metal salt is subjected to at least one particle size reduction step using equipment which comprises one or more of a centrifugal pump, grinder, drop-down blender, particle size reduction homogenizer or delumper.

[c31] 31. The method according to claim 30 wherein the particle size reduction step is performed on a slurry of alkali metal salt in an organic solvent before or during transfer of alkali metal salt to a polymerization vessel.

[c32] 32. The method according to claim 27 wherein the slurry of alkali metal salt is prepared by spraying an aqueous solution of alkali metal salt into said organic solvent.

[c33] 33. The method according to claim 32 wherein the alkali metal salt is the disodium salt of bisphenol A.

[c34] 34. The method according to claim 33 wherein the organic solvent is selected from the group consisting of ortho-dichlorobenzene, toluene and mixtures thereof.

[c35] 35. The method according to claim 1 comprising embodiment F-1.

[c36] 36. The method according to claim 35 wherein the alkali metal salt is stoichiometrically pure.

[c37] 37. The method according to claim 1 comprising embodiment F-2.

[c38] 38. A method for preparing an aromatic polyetherimide which comprises contacting, in o-dichlorobenzene or anisole as solvent, substantially equimolar amounts of bisphenol A disodium salt and at least one bis(N-(chlorophthalimido))aromatic compound selected from the group consisting of 1,3-

bis[N-(4-chlorophthalimido)]-benzene, 1,4-bis[N-(4-chlorophthalimido)]benzene, 4,4'-bis[N-(3-chlorophthalimido)]phenyl ether and 4,4'-bis[N-(4-chlorophthalimido)]phenyl ether, in the presence of a hexaalkylguanidinium chloride as phase transfer catalyst and, optionally, at least one chain termination agent selected from the group consisting of 4-chloro-N-methylphthalimide, 4-chloro-N-butylphthalimide, 4-chloro-N-octadecylphthalimide, 3-chloro-N-methylphthalimide, 3-chloro-N-butylphthalimide, 3-chloro-N-octadecylphthalimide, 4-chloro-N-phenylphthalimide, 3-chloro-N-phenylphthalimide, 1-N-(4-chlorophthalimido)-3-(N-phthalimido)benzene, 1-N-(3-chlorophthalimido)-3-(N-phthalimido)benzene, 4-N-(3-chlorophthalimido)phenyl-4'-(N-phthalimido)phenyl ether, 4-N-(4-chlorophthalimido)phenyl-4'-(N-phthalimido)phenyl ether, or the corresponding isomers derived from 3,4'-diaminodiphenyl ether; said method further comprising at least one of the following embodiments:

(A) drying, by distillation, the bisphenol A disodium salt, in combination with a portion of solvent, to a water content of at most about 20 ppm, and drying, by distillation, the bis(N-(chlorophthalimido))aromatic compound, in combination with a portion of solvent and optionally with chain termination agent, to a water content of at most about 20 ppm;

(B) starting the reaction by addition of phase transfer catalyst wherein the polymer solids level in said solvent is at a value of at least about 15% and then concentrating the mixture during reaction by distillation until the said value is in the range of between about 25% polymer solids level and about 60% polymer solids level;

(C) maintaining the combined level of said bisphenol A disodium salt and bis(N-(chlorophthalimido))aromatic compound in said solvent at a value in the range of between about 25% polymer solids level and about 60% polymer solids level;

(D) beginning said contact using a molar excess of said bis(N-(chlorophthalimido))aromatic compound in the range of between about 0.75% and about 3% and subsequently adding bisphenol A disodium salt at least once to afford a polyetherimide of a desired molecular weight;

(E) employing bisphenol A disodium salt having less than about 25% of particles with a diameter of greater than about 200 nm; and

(F) employing at least one of

(1) bisphenol A disodium salt which is stoichiometrically pure, and

(2) bis(N-(chlorophthalimido))aromatic compound which is stoichiometrically pure or contains excess anhydride groups in a proportion up to about 0.5 mole %, contains phthalides in a proportion no greater than about 1000 ppm, and contains chlorobenzoic acids in a proportion no greater than 0.15 mole %.

[c39] 39. The method according to claim 38 wherein embodiment A is employed and the bis(N-(chlorophthalimido))aromatic compound, at least a portion of solvent and at least a portion of hexaalkylguanidinium chloride, optionally predried separately, are combined and, optionally, further dried by distillation until the value of about 20 ppm water or less is attained; followed by addition of dry bisphenol A disodium salt to the mixture, wherein the initial solids level of the mixture is at least about 15% and the solids level following complete addition of salt and optional concentration is in a range of between about 15% and about 35%.

[c40] 40. The method of claim 38 wherein each of embodiments A-F is employed.